Application Note SI-02297

EPA 521: Determination of Nitrosamines in Drinking Water by GC with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (CI/MS/MS) Using the 220-MS Ion Trap and V:Results™ GC/MS Software

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Introduction

This application note provides procedures for the determination of nitrosamines in finished drinking water. The method may be applicable to untreated source waters and other types of water samples. The method includes the following compounds:

- N-Nitrosodimethylamine (NDMA)
- N-Nitrosomethylethylamine (NMEA)
- N-Nitrosodiethylamine (NDEA)
- N-Nitrosodi-n-propylamine (NDPA)
- N-Nitrosodi-n-butylamine (NDBA)
- N-Nitrosopyrollidine (NPYR)
- N-Nitrosopiperidine (NPIP)

This note provides a basic overview to rapidly set up the Varian 220-MS Ion Trap GC/MS system for the analysis of these seven compounds in the MS/MS configuration.

Instrumentation

- Varian 220-MS Ion Trap Mass Spectrometer with 450-GC Gas Chromatograph
- Varian 1079 Programmable Temperature Vaporizing Injector (PTV) with Siltek™ frit insert (Part No. RT217092145)
- Varian CP-8400 AutoSampler
- Varian V:Results GC/MS software

Initial Calibration

Calibration solutions of 0.5, 1, 2, 5, 10, 20, and 50 ppb are used for all analytes. Both quadratic and linear fits are allowed. The %RSD for each analyte should be less than 30% in order to use the mean response factors for calculations. The %RSD of replicate analyses must be ≤ 20% for all method analytes. The acceptance criteria for initial calibration involves calculating each CAL standard and matching it against the calibration curves. At the highest point, CAL standards must fall between 70-130% of their true value, and at the lowest point, fall between 50-150% of their true value.

GC Conditions

Column:	FactorFour™ VF-624ms 60 m × 0.25 mm x 1.4 µm (Part No. CP9103)
GC Conditions:	35 °C for 2.5 min, to 100 °C at 10 °C/min, to 215 °C for 5.5 min at 5 °C/min, and to 255 °C for 1.0 min at 25 °C/min
Inj. Volume:	20 µL
Inj. Temp:	40 °C for 0.5 min, to 270 °C at 200 °C/min for 34 min
Inj. Split Vent:	Initial split on at 25:1, split off at 0.42 min, and then split on at 3.5 min with 50:1 split

MS Conditions

Target TIC:	5000 counts
µscans Averaged:	3
Emission Current:	40 µA
Multiplier Offset:	100 V
Manifold Temp:	40 °C
Transfer line Temp:	250 °C
Ion Trap Temp:	150 °C

MS/MS Parameters

Time (min)	Precursor Ion (*m/z*)	Excitation Storage	Excitation Amplitude	Product Ions (*m/z*)
13-16.6	75	35	0.5	44+47
16.5-18.3	89	35	0.5	61
18.3-23.0	103	38	0.5	75
23.0-24.4	145 131	50 50	0.5 0.5	97 89
24.4-25.4	101	39	0.48	55
25.4-28.2	115	45	0.48	69
28.2-33.0	159	52	0.48	57+103

Results and Discussion

A typical total ion chromatogram (TIC) is shown in Figure 1.

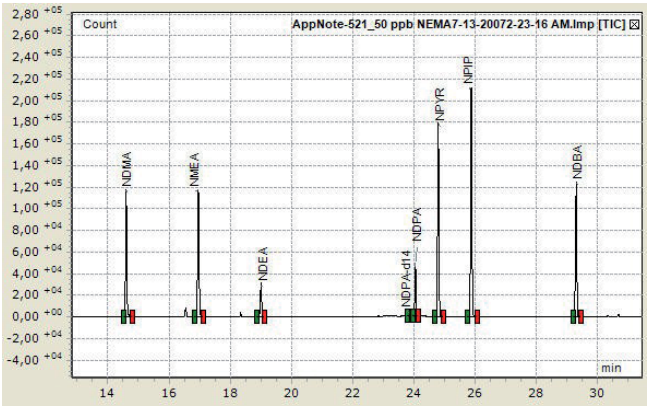

Figure 1. TIC of nitrosamines at 50 ppb, Varian 220-MS GC/MS.

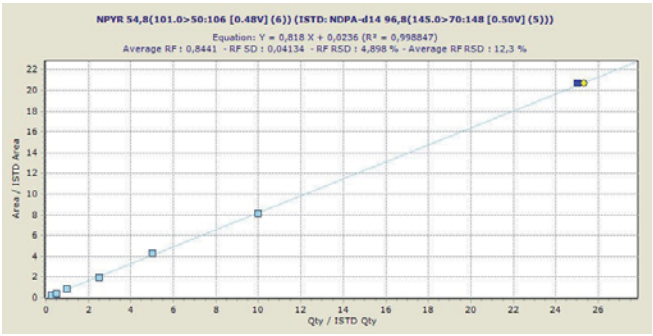

Figure 2. Calibration of N-Nitrosopyrollidine (NPYR) from 0.5 to 50 ppb.

All compounds showed excellent calibration coefficient and relative standard deviation at concentrations ranging from 0.5 ppb to 50 ppb (Table 1). An example of calibration for NPYR is shown in Figure 2. The average r^2 and %RSD of all seven compounds are 0.9945 and 11.23%, respectively.

Table 1. Calibration data of seven nitrosamines.

Compound Name	FT	Correlation Coefficient (r^2)	Average RRF	%RSD
NDMA	14.61	0.9856	0.484	17.48
NMEA	16.96	0.9973	0.704	11.17
NDEA	18.99	0.9967	0.167	11.47
NDPA-d14	23.84			
NDPA	24.05	0.9879	0.261	9.66
NPYR	24.79	0.9988	0.844	4.90
NPIP	25.87	0.9954	1.109	9.92
NDBA	29.29	0.9996	0.590	14.04
Average		0.9945		11.23

The accuracy and precision of all seven nitrosamines were determined at 1 ppb from eleven measurements. The results are listed in Table 2. The precision is significantly below 20%, and accuracy easily exceeds 70% recovery, as required by the method.

Table 2. Precision and accuracy data at concentration of 1 ppb (n = 11).

Compound Name	Measured Concentrations (ppb)	Accuracy (r^2)	Precision (%RSD)
NDMA	0.928	92.8	7.53
NMEA	0.980	98.0	11.81
NDEA	1.005	100.5	3.09
NDPA	1.035	103.5	9.40
NPYR	0.895	89.5	4.54
NPIP	0.921	92.1	4.38
NDBA	0.908	90.8	4.26

The measured concentrations and their differences to true values of each analytes at 0.5, 2 and 20 ppb are listed in Table 3. Results exceed calibration acceptable criteria of ≤ 30% deviation for each concentration, except the lowest point, requiring ≤ 50% deviation.

Table 3. Calibration criteria at 0.5, 2, and 20 ppb concentration.

	0.5 ppb		2 ppb		20 ppb	
Compound Name	Measured Concentrations (ppb)	Deviation (%)	Measured Concentrations (ppb)	Deviation (%)	Measured Concentrations (ppb)	Deviation (%)
NDMA	0.519	3.80	1.848	-7.60	18.666	-6.67
NMEA	0.502	0.40	1.928	-3.60	20.078	0.39
NDEA	0.506	1.20	1.981	-0.95	20.283	1.42
NDPA	0.516	3.20	1.906	-4.70	20.088	0.44
NPYR	0.503	0.60	2.024	1.20	19.797	-1.02
NPIP	0.492	-1.60	2.177	8.85	19.255	-3.73
NDBA	0.499	-0.20	2.043	2.15	19.462	-2.69

Conclusion

Varian 220-MS Ion Trap GC/MS in MS/MS configuration showed excellent accuracy and repeatability for all seven nitrosamine compounds. The entire GC/MS system is proven to exceed the performance required in US EPA Method 521 and validated to meet all of the QC criteria outlined in the method.

These data represent typical results.
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